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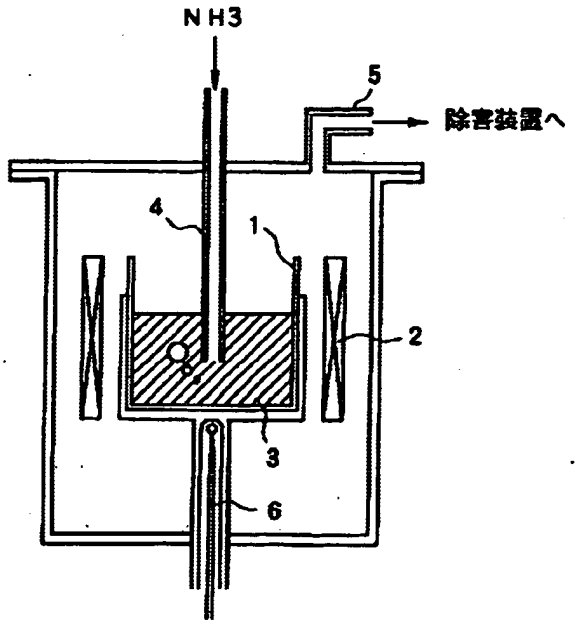
(54)【発明の名称】　窒化物結晶の製造方法、混合物、液相成長方法、窒化物結晶、窒化物結晶粉末、および気相成長方法

(57)【要約】

【課題】従来大型結晶を得るのが困難であったＧａＮ等のIII 族元素の高純度な窒化物結晶を容易かつ安価に得ることのできる、新規な結晶成長方法を提案することにある。

【解決手段】III 族金属元素を加熱、融解し、得ようとする窒化物の融点以下の温度で、III 族金属元素の融液３に窒素原子を含有するガスNH_3を注入して、III 族金属元素の融液３内で、融液３との濡れ性の高いIII 族の窒化物微結晶を製造する。これにより得られるIII 族の窒化物微結晶とIII 族金属原料融液の混合物を液相成長法の出発原料に用いるか、前記混合物からIII 族金属原料を除去して得られるIII 族の窒化物粉末を気相成長法の出発原料に用いる。さらに、ガリウム等のIII 族元素の融液中に種結晶または基板結晶を浸漬し、その表面にアンモニア等の窒素を含有するガスの気泡を断続的に接触させて、種結晶または基板結晶の表面でIII 族元素と窒素を含有するガスを反応させ、これによりその表面にIII 族元素の窒化物結晶を成長させる。



【特許請求の範囲】

【請求項１】III 族金属元素を加熱、融解し、得ようとする窒化物の融点以下の温度で、III 族金属元素の融液に窒素原子を含有するガスを注入して、III 族金属元素の融液内でIII 族の窒化物微結晶を製造することを特徴とする窒化物結晶の製造方法。

【請求項２】請求項１記載の窒化物結晶の製造方法において、III 族金属元素に不純物元素を混ぜておくことにより、該不純物元素をドープしたIII 族の窒化物結晶を製造することを特徴とする窒化物結晶の製造方法。

【請求項３】請求項１または２に記載の窒化物結晶の製造方法により得られるIII 族の窒化物微結晶とIII 族金属元素の混合物。

【請求項４】請求項１または２記載の窒化物結晶の製造方法により得られる、III 族の窒化微結晶とIII 族金属元素の混合物を出発原料に用いることを特徴とするIII 族の窒化物結晶の液相成長方法。

【請求項５】請求項１または２記載の窒化物結晶の製造方法により得られる、III 族の窒化物微結晶とIII 族金属元素の混合物を出発原料に用いた液相成長方法で得られるIII 族の窒化物結晶。

【請求項６】請求項１または２記載の窒化物結晶の製造方法により得られる、III 族の窒化物微結晶とIII 族金属元素の混合物から、III 族金属元素を除去して得られるIII 族の窒化物結晶粉末。

【請求項７】請求項６記載のIII 族の窒化物結晶粉末を出発原料に用いることを特徴とするIII 族の窒化物の気相成長方法。

【請求項８】請求項６記載のIII 族の窒化物粉末を出発原料に用いたIII 族窒化物の気相成長方法で得られるII I 族の窒化物結晶。

【請求項９】請求項６記載のIII 族の窒化物結晶粉末を溶融、再凝固または焼結することを特徴とするIII 族の窒化物結晶の製造方法。

【請求項１０】請求項６記載のIII 族の窒化物結晶粉末を、溶融、再凝固または焼結して得られたIII 族の窒化物結晶。

【請求項１１】請求項１または２記載の窒化物結晶の製造方法において、上記III 族元素がＡｌ、Ｇａ、Ｉｎのうちいずれかであり、かつ上記窒素原子を含有するガスがアンモニアガスであることを特徴とする窒化物結晶の製造方法。

【請求項１２】加熱、融解したIII 族元素中に種結晶を浸漬し、III 族元素中で該種結晶表面に窒素原子を含有するガスの気泡を断続的に接触させることにより、該種結晶表面にIII 族元素の窒化物結晶を成長させることを特徴とする窒化物結晶の製造方法。

【請求項１３】加熱、融解したIII 族元素中に基板結晶を浸漬し、III 族元素中で該基板結晶表面に窒素原子を含有するガスの気泡を断続的に接触させることにより、該基板結晶表面にIII 族元素の窒化物単結晶をエピタキシャル成長させることを特徴とする窒化物結晶の製造方法。

【請求項１４】請求項１２又は１３記載の窒化物結晶の製造方法において、前記III 族元素がＡｌ、Ｇａ、Ｉｎのうちのいずれかであり、かつ前記窒素原子を含有するガス物質がアンモニアガスであることを特徴とする窒化物結晶の製造方法。

【請求項１５】請求項１２又は１３記載の窒化物結晶の製造方法において、前記III 族元素融液の温度が、成長させる窒化物結晶の融点よりも低いことを特徴とする窒化物結晶の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、III 族元素の窒化物結晶、特にＧａＮ、ＡｌＮ、ＩｎＮ等の窒化物結晶の製造方法、混合物、液相成長方法、窒化物結晶、窒化物結晶粉末、及び気相成長方法に関するものである。

【０００２】

【従来の技術】いまだかって、ＧａＮ、ＡｌＮ、ＩｎＮ等の大型のIII 族窒化物結晶を容易に製造することのできる方法は存在していない。ＧａＮバルク結晶ができれば、青色レーザダイオードの実現等にとり、そのインパクトは計り知れない。また、ワイドキャップ半導体材料のバルク結晶は、２１世紀に入ると本格化するものと思われる。

【０００３】ＧａＮの結晶粉末を製造する方法としては、Ga_2O_3 等のＧａの酸化物をアンモニアと反応させて製造する方法が実用化されており、これによって製造された粉末が試薬用に市販される。

【０００４】III 族窒化物結晶のバルク結晶を容易に製造することのできる方法は、未だ開発されていない。わずかに、S.Porowskiらによって次の文献が発表されているが、非常に高い圧力を必要とするため、結晶の製造が危険かつ困難である割に、得られた結晶のサイズは数mm程度と小さい。

【０００５】" Prospects for high-pressure crystal growth of III-V nitrides" S.porowski, J. Jun, P. Perlin, I. Grzegory, H. Teisseyre and T. Suski Inst. Phys. Conf. Ser. No. 137 : Chapter 4Paper presented at the 5th SiC and Related Materials Conf., Washington, DC, 1993

ＧａＮに代表されるIII 族窒化物は、融点が非常に高く、また融点以下の温度で昇華、分解が起こるため、その融液を作ることができず、融液からの結晶成長ができない。また、III 族融液に対する溶解度が非常に低いため、溶液からの結晶成長も難しい。これまでに実用化されているIII 族窒化物の結晶成長方法は、ＨＶＰＥ（水素化物気相成長法）、ＭＯＶＰＥ（有機金属気相成長）法、ＭＢＥ（分子線エピタキシー）法の３種の気相エピ

タキシャル成長法だけである。また、これにより製造されたＧａＮ系のＬＥＤが市販されるに到っている。ＭＯＶＰＥ法によるＧａＮの結晶成長の例としては、次のような文献が発表されている。

【０００６】" Novel metalorganic chemical vapor deposition system for GaN growth" S. Nakamura、Y. Harada and M. Seno 、Appl. Phys. Lett. 58(18)6, 1991

【０００７】

【発明が解決しようとする課題】ＧａＮに代表されるIII 族元素の窒化物結晶は、近年青色発光素子用の材料として注目を集めている。素子を作成するためには、基板の上に例えばＧａＮ結晶等をエピタキシャル成長させる必要がある。このエピタキシャル成長においては、成長する結晶中の歪みの発生を防止するために、基板となる結晶の格子定数や熱膨張率が、その上に成長する結晶と同一であることが理想的である。しかし、これまで基板として使用できるような窒化物のバルク結晶は得られておらず、やむなく格子定数の異なるサファイア基板等で代用し、その上にエピタキシャル成長してきた。

【０００８】エピタキシャル成長法としては、現在ＭＯＶＰＥ法が主流となっているが、原料の、有機金属は、発火しやすく危険であり、また高価であること。さらに、大がかりで複雑、高価な成長装置を必要とすること。成長結晶中に不純物として水素が入るのが避けられず、これが原因となってｐ型結晶の高キャリア化が難しいなどの問題がある。

【０００９】したがってｐ型結晶を高キャリア化するため、ｐ型誘電層を素子表面に持ってきて、窒化物結晶処理を施す必要がある。ｐ型誘電層を素子表面に持ってくる必要性があるため、素子構造の設計の自由度が狭かった。

【００１０】他のエピタキシャル成長法として、III 族元素の溶媒にIII 族窒化物結晶を溶質として溶かし、ＬＰＥ（液相エピタキシャル）成長させる方法がある。しかし、従来市販されていたIII 族窒化物結晶は、例えばＧａＮであればGa_2O_3 等のＧａの酸化物をアンモニアと反応させて製造した微粉末であり、その形状に起因してＧａＮ結晶の表面がＧａと濡れにくく、したがってＧａに解けにくいという問題があった。

【００１１】窒化物結晶の粉体は、蛍光材料としてや、ＧａＡｓ、ＧａＰ等の液相エピタキシャル成長におけるドーパント材料としても応用が期待される。しかし、従来市販されていたＧａＮ結晶粉末は、高価な割に純度が低く、気相成長用の出発原料には不向きであった。また、その形状に起因して半導体融液に解けにくいため、液相成長用の原料やドーパント原料としても使いにくいという問題があった。

【００１２】本発明の目的は、前述のような従来技術の問題点を解消し、ＧａＮ等の高純度なIII 族元素の窒化物結晶を容易かつ安価に得ることのできる新規な窒化物結晶の製造方法、混合物、気相成長方法、窒化物結晶、窒化物結晶粉末、および気相成長方法を提案することにある。

【００１３】また、本発明の他の目的は、これまで得られていなかったＧａＮ等のIII 族元素の窒化物結晶のバルク結晶を、容易に成長させることのできる新規な結晶成長方法と、簡便かつ安全にIII 族窒化物結晶のエピタキシャル成長を行うことのできる新規な結晶成長方法を提案することにある。

【００１４】

【課題を解決するための手段】本発明の第１の要点は、大きく分けて３つある。

【００１５】① アンモニア等の窒素を含有するガスを高温のＧａ等のIII 族元素の融液に注入することで反応させる。これにより、III 族元素の融液中にIII 族窒化物の微結晶が大量に浮いてくる。

【００１６】② こうして得られたIII 族元素とIII 族窒化物微結晶の混合物を原料にして、III 族窒化物結晶の液相エピタキシャル成長を行う。上述の方法で得られたIII 族元素窒化物微結晶はIII 族元素融液とのなじみが良く、III 族窒化物微結晶をIII 族元素融液に容易に溶解させることができる。

【００１７】③ 上記の混合物から酸洗浄等でIII 族元素を除去して得られるIII 族窒化物微結晶を原料にして、III 族窒化物結晶の気相成長や融解、焼結結晶を製造する。この方法で得られた原料は、高純度かつ安価という特徴がある。

【００１８】詳述するに、III 族融液にＶ族元素の蒸気を注入してIII －Ｖ族化合物を合成する手法は、インジェクション（injection)法と呼ばれ、公知の技術である。例えば、III －Ｖ族化合物半導体の１つであるＩｎＰの多結晶を合成した例として、次のような学会報告もある。

【００１９】" P-injection 法によるＩｎＰ多結晶の大量合成"、
柴田他、第３４回応用物理学関係連合講演会（1987）28 p-Z-1

しかし、injection 法は、III 族融液を合成するIII －Ｖ族化合物の融点以上に加熱し、そこへＶ族元素の蒸気を注入して、一旦、III －Ｖ族化合物の融液を作り、これを冷却して結晶を作製する、いわゆる融液成長法の一つであるのに対し、本発明の請求項１にかかる窒化物の合成法は、合成する窒化物の融点よりもずっと低い温度でIII 族融液中に窒素を含有するガスを注入し、液相のIII 族元素と気相のＶ族元素を反応させて、III 族元素融液中で固相のIII 族窒化物結晶を直接生成する（窒化物の融液はできない）という点で従来のinjection 法とは全く異なる新しい合成法である。これは、窒化物のIII 族元素融液への溶解度が非常に低いという特徴を逆手に取って、積極的に利用したものである。

【００２０】この請求項１記載の窒化物結晶の製造方法において、III 族金属元素に不純物元素を混ぜておくことにより、不純物をドープしたIII 族の窒化物結晶を製造することができる（請求項２）。そしてこの請求項１または２記載の窒化物結晶の製造方法により、III 族の窒化物粉末とIII 族金属原料の混合物が得られる（請求項３）。

【００２１】本発明の請求項４にかかるIII 族窒化物結晶とIII 族金属原料の混合物は、III 族窒化物結晶が微結晶であるにもかかわらず、その表面が完全にIII 族金属原料で濡れている点に大きな特徴がある。液相成長用の原料や、ドーパントに結晶微粉末を加える際、その体積に比して表面積の大きな微粉末は、III 族融液になじみにくく、したがって非常に溶解しにくいという問題がある。特に、飽和溶解度の低い窒化物結晶においては、この溶けにくさが結晶成長にとって致命的な欠点となる。従来市販されているようなIII 族窒化物は、ほとんど微粉末状態であり、一様に上述の欠点を有していた。本発明にかかるIII 族窒化物微結晶粉末とIII 族金属原料の混合物は、窒化物結晶がIII 族融液中で合成されるため、その表面が完全にIII 族金属原料で覆われており、液相成長原料として用いるとき、非常に溶解しやすく、従来の原料に較べ、容易に飽和溶解度に達しさせることができる。その結果、エピタキシャル成長の制御性、再現性が飛躍的に向上し、高純度なIII 族の窒化物結晶が得られる（請求項５）。

【００２２】また、従来のIII 族窒化物合成法では、原料にIII 族の酸化物や塩化物を用いるため、合成した窒化物粉末から未反応物を除去する工程が必ず必要であった。本発明の請求項１、２および４にかかる製造方法では、原料に酸化物や塩化物を用いていないので、未反応物が液相成長時の不純物にならず、したがって液相成長の原料に用いる際にIII 族窒化物だけを抽出することなしに、該混合物を直接液相成長の原料とすることができる。この抽出工程を省略できることは、工程の大幅短縮につながるだけでなく、抽出工程で発生しがちな原料の汚染を無くすことができ、高純度な液相成長が可能となる。

【００２３】上記請求項３～５に記載の発明は液相成長方法に関するものであるが、本発明は、気相成長方法にも適用できる。すなわち、請求項６に記載の発明は、請求項１または２に記載の窒化物結晶の製造方法により得られるIII 族の窒化物微結晶とIII 族金属原料の混合物からIII 族金属原料を除去して得られるIII 族の窒化物結晶粉末である。この窒化物結晶粉末を出発原料に用いてIII 族の窒化物結晶を気相成長させることができる（請求項７）、その気相成長によりIII 族の窒化物結晶を得ることができる（請求項８）。

【００２４】また請求項９に記載の発明は、請求項６記載のIII 族の窒化物粉末を、溶融、再凝固または焼結するIII 族の窒化物結晶の製造方法であり、請求項１０に記載の発明は、その製造方法により得られたIII 族の窒化物結晶である。

【００２５】なお、請求項１または２記載の窒化物結晶の製造方法において、上記III 族元素がＡｌ、Ｇａ、Ｉｎのうちいずれかであり、かつ上記窒素原子を含有するガスをアンモニアガスとすることもできる（請求項１１）。さらに、請求項３～１０に記載の発明においても、III 族元素をＡｌ、Ｇａ、Ｉｎのうちいずれかとすることができる。

【００２６】本発明の第２の要点は、ガリウム等のIII 族元素の融液中に種結晶または基板結晶を浸漬し、その表面にアンモニア等の窒素を含有するガスの気泡を断続的に接触させて、種結晶または基板結晶の表面でIII 族元素と窒素を含有するガスを反応させることにより、その表面にIII 族元素の窒化物結晶を成長させる方法である。

【００２７】この窒化物結晶の成長法も、合成する窒化物の融点よりもずっと低い温度で、III 族融液中に窒素を含有するガスを注入し、液相のIII 族元素と気相のV族元素を反応させて、III 族元素融液中で固相のIII 族窒化物結晶を直接生成すること（窒化物の融液はできない）を前提とする。これは、窒化物のIII 族元素融液への溶解度が非常に低いという特徴を逆手に取って、積極的に利用したものであり、この前提自体が、既に述べたように、上記injection 法のような融液成長法とは全く異なる新しい概念に基づく結晶成長法である。

【００２８】ガリウム、アルミニウム、インジウム等のIII 族元素とアンモニア、ヒドラジン等の窒素を含有するガスは、窒化物の融点（例えばＧａＮであれば２０００℃以上と言われている）に比べればかなり低い数百～１０００℃程度の温度で反応し、III 族窒化物を生成することが知られている。例えば、次のような報告がある。

【００２９】" Crystal growth of GaN by reaction between Ga and NH_3 "
D.Elwell et.al., J.Crystal Growth 66 (1984) 45-54

しかし、生成したＧａＮはIII 族融液には溶解せず、微粉末となってIII 族融液の表面に析出するのみである。

【００３０】請求項１２又は１３に記載の窒化物結晶の製造方法では、ガリウム等のIII 族元素の融液中に種結晶または基板結晶を浸漬し、その表面にアンモニア等の窒素を含有するガスの気泡を断続的に接触させる。種結晶または基板結晶の表面でIII 族元素と窒素を含有するガスを反応させることにより、種結晶または基板結晶の表面に結合したIII 族原子を窒化させ、下地に対して窒化物結晶を成長させていくことができる。この反応を連続的に行えば、エピタキシャル膜の成長や、バルク結晶の成長を行うことができる。

【００３１】なお、請求項１２または１３記載の窒化物結晶の製造方法において、上記ＩＩＩ族元素がＡｌ、Ｇａ、Ｉｎのうちいずれかであり、かつ上記窒素原子を含有するガスをアンモニアガスとすることもできる（請求項１４）。さらに、請求項１２または１３に記載の窒化物結晶の製造方法において、前記ＩＩＩ　族元素融液の温度は、成長させる窒化物結晶の融点よりも低くする（請求項１５）。

【００３２】

【発明の実施の形態】以下、本発明の実施の形態を、実施例を中心に説明する。

【００３３】（実施例１）本発明の一実施例として、図１に示すような装置を製作した。この装置を用いて、ＧａＮ微結晶の合成を行った例を述べる。

【００３４】内径７０mm高さ１５０mmの石英ルツボ１にＧａを３０００ｇ収容し、ヒータ２でＧａを９５０℃まで加熱してＧａ融液３を形成した。続いて、ガス導入配管４を使ってＧａ融液３中にアンモニアガスを０．５１／min の流量で５時間吹き込み続けた。融液３に吹き込まれたガスは、融液と反応してＧａＮ微結晶を生成し、微結晶は融液表面に浮かび上がった。反応に寄与しなかったアンモニアガスは、泡となって融液３内を通過し、容器上部の空間に出て、排気管５を通じて容器外に排出される。排出されたアンモニアガスは、湿式の除害装置を通して大気に放出した。５時間のガス注入を行った後、注入するガスを窒素に切り替え、Ｇａ融液を室温まで冷却した。

【００３５】冷却したＧａ融液を容器から取り出して観察したところ、Ｇａ融液の上部にＧａＮの微結晶が大量に浮かんでいた。ＧａＮ微結晶の表面は、完全にＧａ融液と濡れた状態であった。Ｇａ融液は、合成作業の前後で１０．２ｇの重量増加が認められた。ここから計算すると、６１ｇのＧａＮ微結晶が合成できたことになる。

【００３６】（実施例２）実施例１のようにしてＧａＮ微結晶を合成し、Ｇａ融液の上部に浮かぶＧａ融液とＧａＮ微結晶の混合物を原料に用いて、スライドボート法でＧａＮの液相エピタキシャル成長を行った。成長に用いた装置の断面模式図を図２に示す。グラファイトボート１１に、原料１２としてＧａ融液とＧａＮ微結晶の混合物を２０ｇ入れた。スライドボート１７には、２５mm角のｃ面サファイア基板１６をセットした。石英反応管１４内は、窒素ガス気流雰囲気とし、ヒータ１３で熱電対１５出力が１１５０℃になるまで原料を加熱した。この状態で４時間放置した後、温度を１１００℃に下げ、操作棒１８を引いてスライドボート１７を移動し、サファイア基板１６を原料１２と接触させた。これ以降は、原料温度を毎分１℃割合で６００℃まで下げ、操作棒１８を押してスライドボート１７を元の位置に戻し、基板１６と原料１２を切り離した。その後ヒータ電源を切って室温まで冷却した。液相エピタキシャル成長時の温度プログラムを図３に示す。

【００３７】成長の終わった基板を取り出して表面及び断面を観察した。サファイア基板の表面には透明な膜が成長していた。断面のＳＥＭ観察から求めた膜厚は４．２μmであった。成長した膜の室温でのフォトルミネッセンス測定結果を図４に示す。ＧａＮのバンド端発光に対応する３６０nmの鋭い発光ピークが観察され、成長した膜が良質なＧａＮ膜であることを確認した。成長した膜の電気特性を、ファンデァポー（Van der Pauw）法で測定したところ、キャリア濃度は$1\times10^{17}cm^{-3}$、移動度は５２０cm^2／Ｖ・sec と、良好な特性を示した。

【００３８】（実施例３）実施例１と同様の方法で、あらかじめ原料Ｇａに２０mgのＳｉを入れてＧａＮ微結晶を合成し、得られたＧａ融液とＧａＮ微結晶の混合物を原料に用いて、実施例２と同様のスライドボート法でＧａＮの液相エピタキシャル成長を行った。

【００３９】得られたＧａＮ膜の室温でのフォトルミネッセンス測定結果を、図５に示す。ＳｉドープＧａＮの発光に対応する３６９nmの鋭い発光ピークが観察され、成長した膜にＳｉがドープされていることを確認した。成長した膜のキャリア濃度を、ファンデァポー法で測定したところ、ｎ型の$6\times10^{18}cm^{-3}$であった。

【００４０】（実施例４）実施例１と同様の方法で、あらかじめ原料Ｇａに７mgのＭｇを入れてＧａＮ微結晶を合成し、得られたＧａ融液とＧａＮ微結晶の混合物を原料に用いて、実施例２と同様のスライドボート法でＧａＮの液相エピタキシャル成長を行った。

【００４１】得られたＧａＮ膜の室温でのフォトルミネッセンス測定結果を、図６に示す。ＭｇドープＧａＮの発光に対応する４４５nmの発光ピークが観察され、成長した膜にＭｇがドープされていることを確認した。成長した膜のキャリア濃度を、ファンデァポー法で測定したところ、ｐ型の$5\times10^{17}cm^{-3}$であった。本方法で得られたＭｇドープＧａＮ膜は、ＭＯＶＰＥ成長で得られた膜が熱処理を加えなければ結晶中のＭｇが活性化されず、ｐ型電気特性を示さないのに対し、アズグロウンの状態で良好なｐ型の電気特性を示した。これは、Ｍｇの活性化を妨げる水素原子の混入がなかったためと考えられる。

【００４２】（実施例５）実施例１と同様の方法で合成した、アンドープＧａＮ微結晶と金属Ｇａの混合物を採取し、これに塩酸と過酸化水素水を加えてＧａだけを溶解した後、濾紙で濾してＧａＮ微結晶だけを取り出した。濾過した粉末は純水で十分に洗浄した後、真空高温槽内で乾燥した。その結果、灰白色をした粉末が６１ｇ得られた。この粉末を顕微鏡で観察したところ、粒径～１０μm程度の６角柱を基本とする微結晶からなっていた。本粉末の室温フォトルミネッセンス測定結果を図７に示す。ＧａＮのバンド端発光に対応する３６０nmの鋭い発光ピークが観察され、得られた微結晶が良質なＧａ

Nであることを確認した。得られた粉末中に混入する可能性のある不純物の濃度を二次イオン質量分析法（ＳＩＭＳ）で調べたが、石英容器からの混入と思われるＳｉが$5\times10^{15}cm^{-3}$程度検出された以外、すべて検出限界以下であった。

【００４３】（実施例６）実施例５で得られたＧａＮ微結晶粉末を原料に用いて、図８に示すような装置でＧａＮの気相エピタキシャル成長を行った。直径５０㎜の石英ルツボ２３に、原料としてＧａＮ微結晶粉末２６を２５ｇ入れ、これをグラファイトサセプタ２５で支持して石英容器２１内にセットした。一方、２５㎜角のｃ面サファイア基板２８をグラファイト製の基板ホルダー２２に固定し、基板表面が原料２６と対向するように、基板を石英ルツボ２３内に吊り下げた。この状態で石英容器２１内をアンモニアガス雰囲気に置換し、続けてアンモニアガスを毎分０．５リッター流しながら、ヒータ２４で原料を加熱した。加熱は、ルツボ下に配した熱電対２７の出力で、１１００℃となるように制御した。この時、基板２８の表面温度は約８５０℃になっていた。結晶成長は、原料を加熱した状態で２４時間保持して昇華させることにより行った。

【００４４】取り出したサファイア基板の表面には、透明なＧａＮの膜が成長していた。ＧａＮ膜の表面を顕微鏡で観察すると、三角～六角形をしたモルフォロジが観察された。成長した膜の平均厚さは、約４００μｍであった。成長した膜の電気特性を、ファンデアポー法で測定したところ、キャリア濃度$2\times10^{17}cm^{-3}$、移動度は$490cm^2$／Ｖ・sec と、良好な特性を示した。

【００４５】（実施例７）実施例１と同様の方法で、Ｇａの代わりにＩｎを用い、ＩｎＮの合成を行った。合成温度を６００℃とした以外は、実施例１と同一条件である。合成の終わったＩｎを１８０℃まで冷却し、Ｉｎが凝固しないうちに、Ｉｎ融液の上部に浮かんだＩｎＮ微結晶と金属Ｉｎの混合物を取り出した。

【００４６】この混合物に塩酸と過酸化水素水を加えてＩｎだけを溶解した後、濾紙で濾してＩｎＮ微結晶だけを取り出した。濾過した粉末は純水で十分に洗浄した後、真空高温槽内で乾燥した。その結果、薄い灰白色をした粉末約２００ｇ得られた。この粉末を顕微鏡で観察したところ、粒径～８μｍ程度の、６角柱を基本とする微結晶からなっていた。得られた粉末のフォトルミスペクトルを測定したところ、ＩｎＮのバンド端発光に相当する６５０㎚の発光が観察された。

【００４７】（変形例）上記実施例ではＧａＮの結晶成長を中心に、さらにＩｎＮの結晶成長についても述べたが、その他ＡｌＮや、ＡｌＮまたはＩｎＮの混晶であるＡｌＧａＮ、ＧａＩｎＮなどの結晶成長にも適用できる。

【００４８】窒素を含むガスとしては、アンモニアの他にヒドラジン、モノメチルヒドラジンなどの利用が考えられる。

【００４９】液相成長の実施例は大気圧下での結晶成長について述べたが、窒素またはアンモニア雰囲気の高圧下で行えば、さらに結晶成長速度を上げることができる。

【００５０】液相成長、気相成長の実施例は、サファイア基板上へのエピタキシャル成長について述べたが、他の基板を用いたエピタキシャル成長や、さらに窒化物のバルク結晶成長への応用展開も可能である。

【００５１】合成で得られる窒化物微結晶の収率ならびに粒径は、III 族融液中に注入されたアンモニア等のガスの滞在時間によって制御することが可能である。したがって、ガスの注入管の先端形状を変えたり、融液中に、石英細工などでガスの気泡が通る道を設けるなどの変形例が考えられる。

【００５２】（他の実施形態）本発明により得られた窒化物微結晶は、半導体材料や蛍光体材料として広く応用が可能である。特に、本発明の１つにかかる液相成長方法は、紫外～黄色の発光素子の製造に応用すると効果的である。

【００５３】例えば、実施例２で述べた液相成長装置に原料収納部を２ケ所設けて、一方にＭｇドープＧａＮ原料を、他方にＳｉドープＧａＮ原料を収容すれば、基板上にｐ型とｎ型のＧａＮ膜を連続して成長させることができる。こうして得られたエピタキシャル成長基板にＬＥＤ製造プロセスを施せば、容易にｐｎ接合型の青色ＬＥＤを製造することができる。この方法によれば、従来のＭＯＶＰＥ法よりも簡単かつ安全、安価にＬＥＤを製造することができる。また、従来のＭＯＶＰＥ法成長ＧａＮでは、ｐ型結晶を作製するために後から熱処理を加える必要があり、このため結晶表面が常にｐ型になるように素子構造を設計しなければならないという制約があった。本発明にかかる液相エピタキシャル成長法を用いれば、ｐ型の導電性が熱処理を施さなくとも得られるため、素子の構造設計の裕度が非常に大きくなる。

【００５４】なお、窒化物の合成温度や雰囲気圧力、原料の使用量等は、合成する窒化物の種類や使用する原料の種類によって異なるため、その最適条件を一義的に決めることは困難である。

【００５５】（実施例８）本発明の第８の実施例として、図９に示すような装置を製作した。この装置を用いて、ＧａＮ結晶の成長を行った例を述べる。

【００５６】内径７０㎜高さ２００㎜の石英容器３１に融解したＧａ３３を３０００ｇ収容し、溶融Ｇａ３３中には、一辺６㎜のＳｉＣ単結晶のかけらを種結晶３５として種結晶支持治具３４の先端に取り付け、固定した。この状態で、溶融Ｇａ３３をヒータ３２により加熱し、熱電対３７の出力で１０００℃になるよう制御した。

【００５７】続いて、アンモニアガスを、内径６㎜の石英製アンモニア導入管３６を通じて、石英容器の底から

毎分0．2リットルの割合で76時間導入し続けた。溶融Ga33中に導入されたアンモニアガスは、融液中を気泡となって立ち上った。気泡の数は、毎分約350個であった。融液中を上昇するアンモニアガスの気泡は、種結晶35の表面にぶつかり、種結晶表面で次々とGaN結晶を生成していく。未反応のアンモニアガスは、そのまま気泡として溶融Ga表面まで達し、容器外へと排出される。排出したガスは、湿式のスクラーバーで除害して、大気放出した。アンモニアガスの気泡は、種結晶の表面以外でもGaと反応してGaNを生成した。このGaNは、直径数μm程度の微結晶で、溶融Ga表面に浮き上がってきて、種結晶上の成長には寄与しなかった。

【0058】成長の終わった結晶を冷却し、溶融Ga中から取り出して、表面に付着している金属Gaを塩酸で洗い落とした。その結果、SiCの種結晶上に、直径約10㎜高さ約6㎜の六角柱状のGaN結晶が得られた。得られた結晶は、透明な黄褐色を呈していた。得られた結晶は、X線回折法によりGaN結晶であることを確認した。X線回折ピークの半値幅（FWHM）は、約2min であり、得られた結晶は良好な結晶性を有していると言える。

【0059】図10に、得られた結晶の室温におけるフォトルミネッセンス測定結果を示す。360nmに、アンドープGaNのバンド端発光に対応する鋭い発光ピークが観察され、フォトルミネッセンス測定によっても良質なGaN結晶であることが確認できた。

【0060】（実施例9）本発明の第9の実施例として、図11に示すような装置を製作した。この装置を用いて、GaN結晶のエピタキシャル成長を行った例を述べる。

【0061】内径70㎜高さ150㎜の石英ルツボ45をグラファイトサセプタ44に入れ、ステンレス容器43の内部に設置した。石英ルツボ45の内部には、融解したGa48を3000g収容し、溶融Ga48中には、一辺25㎜のc面サファイア単結晶基板（以下サファイア基板という）49を基板支持治具47の先端に取り付けて浸漬した。サファイア基板49は、溶融Ga中で、数度程度水平から傾けて固定した。また、溶融Ga48中には、先端をJ字型に曲げた石英製のアンモニアガス導入管41を設置した。ガス導入管41の先端は、サファイア基板49の低い方の端の直下になるよう固定した。この状態で、溶融Ga48をヒータ42により加熱し、熱電対46の出力で950℃になるよう制御した。続いて、アンモニアガスを、アンモニア導入管41を通じて、溶融Ga48中に毎分0．1リットルの割合で1時間導入した。導入されたアンモニアガスは、融液中を気泡となって立ち上った。気泡の数は、毎分約200個であった。融液中を上昇したアンモニアガスの気泡は、サファイア基板49の下端にぶつかり基板表面に沿って上昇した後、溶融Ga48表面まで達し、容器外へと排出された。排出したガスは、湿式のスクラーバーで除害して、大気放出した。

【0062】成長の終わった結晶を冷却し、溶融Ga48中から取り出して、表面に付着している金属Gaを塩酸で洗い落とした。その結果、サファイア基板49表面に厚さ約4μmの透明な結晶薄膜が得られた。得られた結晶は、X線回折法によりGaN結晶であることを確認した。X線回折ピークの半値幅（FWHM）は、約5min であった。

【0063】図12に、得られた結晶の室温におけるフォトルミネッセンス測定果を示す。360nmに、アンドープGaNのバンド端発光に対応する鋭い発光ピークが観察され、良質なGaN結晶であることが確認できた。

【0064】なお、窒化物結晶の成長温度や成長中の雰囲気圧力、原料の使用量等は、成長する窒化物の種類や使用する原料の種類によって異なるため、一義的には決められない。

【0065】窒素を含有するガスとして、アンモニアを選ぶのは、化学的にある程度活性で、かつ安全性及び経済性を考慮した結果によるためであるが、原理的にはヒドラジンやモノメチルヒドラジン等のガスも使用が可能である。ただし、これらのガスはアンモニアに較べて遥かに爆発の危険が大きい。

【0066】結晶成長中のIII 族原料温度を、成長する窒化物の融点以下としたのは、成長した結晶が分解したり再融解するのを防ぐためである。

【0067】（変形例）実施例ではGaN の結晶成長について述べたが、InNやAlN、またこれらの混晶であるAlGaN、GaInNなどの結晶成長にも適用できる。さらに、III 族融液中や窒素を含むガス中に、不純物元素を混入することにより、不純物をドープした窒化物結晶も成長が可能である。

【0068】窒素を含むガスとしては、アンモニアの他にヒドラジン、モノメチルヒドラジンなどの利用が考えられる。

【0069】III 族融液中にアンモニア等のガスを導入する管の先端形状は、融液中におけるガスの気泡の大きさや数を制御する目的で、いろいろと変形が考えられる。たとえば、ガス導入管の先端に気泡の吹き出し口を複数個設けたり、ガス導入管の先端に網を設けることができる。

【0070】III 族融液中に種結晶や基板結晶を複数個設置する変形例も考えられる。

【0071】上記図1、図2、図8、図9及び図11に示した実施例では、本発明の要点部分を示す結晶成長容器だけについて述べたが、成長装置の周辺機器として、ガス流量を調節するマスフローコントローラやヒータの温度を自動的にプログラム制御することのできる温調器を組み合わせたシステムを構築すると、より結晶成長の

制御が容易になる。

【００７２】本発明により得られる窒化物結晶は、半導体材料や蛍光体材料として広く応用が可能である。特に、窒化物のバルク単結晶基板は、青色レーザーダイオードを製造する際の基板材料として最適である。

【００７３】

【発明の効果】以上説明したように本発明によれば、次のような優れた効果が得られる。

【００７４】（１）請求項１～請求項２に記載の製造方法によれば、合成する窒化物の融点よりもずっと低い温度でIII 族融液中に窒素を含有するガスを注入し、液相のIII 族元素と気相のＶ族元素を反応させて、III 族元素融液中で固相のIII 族窒化物結晶を直接生成するため、窒化物の融液を作る場合に比べ、簡単な装置で容易にかつ安価に短時間の内に大量に製造することができる。

【００７５】（２）本発明の請求項３にかかるIII 族窒化物微結晶とIII 族金属原料の混合物は、窒化物微結晶がIII 族融液中で合成されるため、その表面が完全にIII 族金属原料で覆われており、この混合物を液相成長原料に使用すれば、非常に溶解しやすく、従来の原料に比べ、容易に飽和溶解度の溶液を得ることができるようになる。その結果、エピタキシャル成長の制御性、再現性が飛躍的に向上する。

【００７６】（３）本発明の請求項４、７、９にかかる成長方法によると、III 族の高純度窒化物半導体結晶を簡単な装置で容易にかつ安価に短時間の内に大量に製造することができる。また、従来ＨＶＰＥ法で使用されてきた塩素などのガスや、ＭＯＶＰＥ法で使用されている有機金属等の危険な原料を使用する必要もなく安全である。また本発明の成長方法によれば、特に従来難しかった窒化物結晶の液相成長や気相成長が容易にできるようになる。その結果、窒化物結晶に特別な処理を施さなくとも高キャリアのｐ型結晶を有するデバイスの製造が容易になり、ｐ型導電層を素子表面に持ってくる必要性がなくなるため、素子構造の設計の自由度が広がる。

【００７７】（４）また、本発明の請求項４、７、９にかかる窒化物の成長方法では、原料に従来のような酸化物や塩化物を用いていないので、未反応物が液相成長時の不純物にならず、したがって液相成長の原料に用いる際にIII 族窒化物だけを抽出することなしに、該混合物を直接液相成長の原料とすることができる。この抽出工程を省略できることは、工程の大幅短縮につながるだけでなく、抽出工程で発生しがちな原料の汚染を無くすことができ、高純度な液相成長が可能となる。

【００７８】（５）さらに、本発明の請求項１２、１３にかかる製造方法によれば、III 族の窒化物半導体結晶、特に従来成長させることができなかったバルク単結晶の成長が可能になる。この結晶を基板に用いれば、青色ＬＥＤの高効率化や長寿命化に有効なだけでなく、未だ実用化に至っていない青色ＬＤの実用化を推進する上にも大きく貢献するものである。また、そのようなIII 族の窒化物半導体結晶を簡単な装置で容易にかつ安価に成長させることができる。加えて、従来ＨＶＰＥ法で使用されてきた塩素などのガスや、ＭＯＶＰＥ法で使用されている有機金属等の危険な原料を使用する必要もなく、安全である。

【図面の簡単な説明】

【図１】本発明の第１及び第７の実施例にかかるＧａＮ結晶合成装置の断面模式図である。

【図２】本発明の第２の実施例にかかるＧａＮ結晶の液相成長装置の断面模式図である。

【図３】本発明の第２の実施例にかかるＧａＮ結晶の液相成長時の温度プログラムを示すグラフである。

【図４】本発明の第２の実施例にかかる液相エピタキシャル成長アンドープＧａＮ結膜の室温でのフォトルミネッセンス測定結果を示す図である。

【図５】本発明の第３の実施例にかかる液相エピタキシャル成長ＳｉドープＧａＮ結晶膜の室温でのフォトルミネッセンス測定結果を示す図である。

【図６】本発明の第４の実施例にかかる液相エピタキシャル成長ＭｇドープＧａＮ結晶膜の室温でのフォトルミネッセンス測定結果を示す図である。

【図７】本発明の第５の実施例にかかるアンドープＧａＮ微結晶粉末の室温でのフォトルミネッセンス測定結果を示す図である。

【図８】本発明の第６の実施例にかかるＧａＮ結晶の気相成長装置の断面模式図である。

【図９】本発明の第８の実施例にかかるＧａＮ結晶成長装置の断面模式図である。

【図１０】本発明の第８の実施例で作製したＧａＮ結晶の室温におけるフォトルミネッセンス測定結果を示した図である。

【図１１】本発明の第９の実施例にかかるＧａＮ結晶エピタキシャル成長装置の断面模式図である。

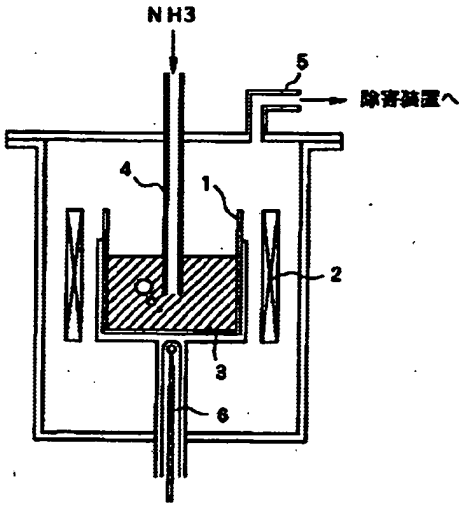
【図１２】本発明の第９の実施例で作製したＧａＮエピタキシャル成長結晶の室温におけるフォトルミネッセンス測定結果を示した図である。

【符号の説明】

１　石英ルツボ
２　ヒータ
３　Ｇａ融液
４　アンモニアガス注入管
５　排気管
６　熱電対
１１　グラファイトボート
１２　ＧａＮ微粉末とＧａの混合物
１３　ヒータ
１４　石英反応管
１５　熱電対

16　サファイア基板
17　グラファイト製スライドボート
18　石英製操作棒
21　石英容器
22　グラファイト製基板ホルダー
23　石英ルツボ
24　ヒータ
25　グラファイト製サセプタ
26　GaN微結晶粉末
27　熱電対
28　サファイア基板
31　石英容器
32　ヒータ
33　溶融Ga
34　種結晶支持治具
35　種結晶
36　アンモニア導入管
37　熱電付

【図1】



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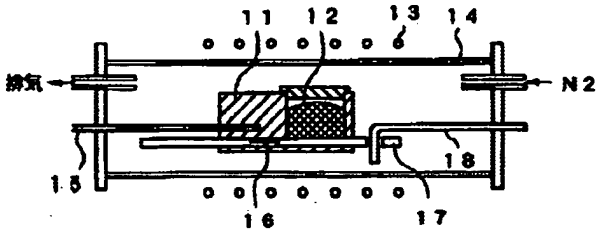

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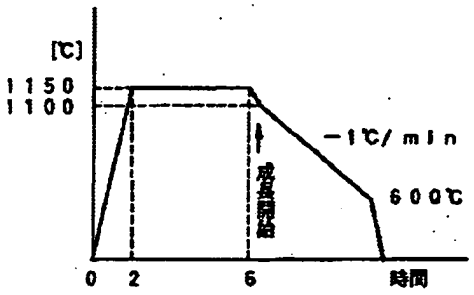

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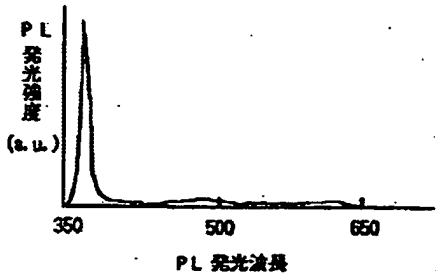

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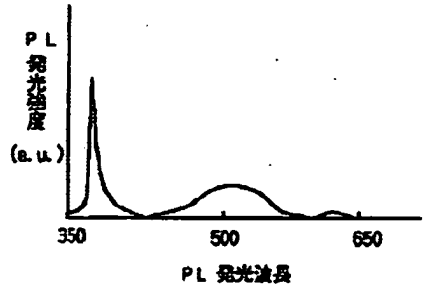

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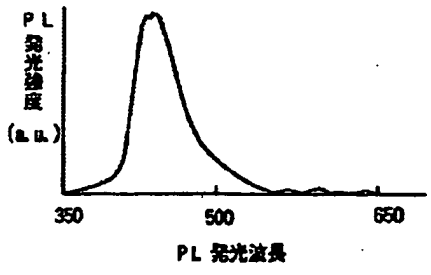

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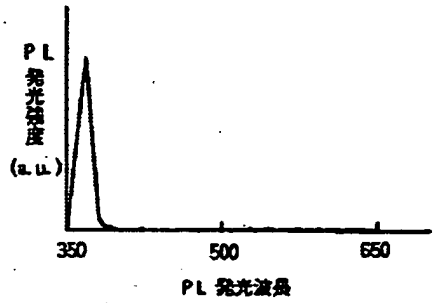

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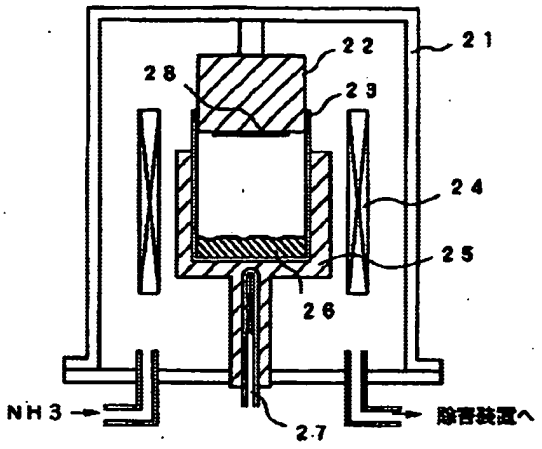

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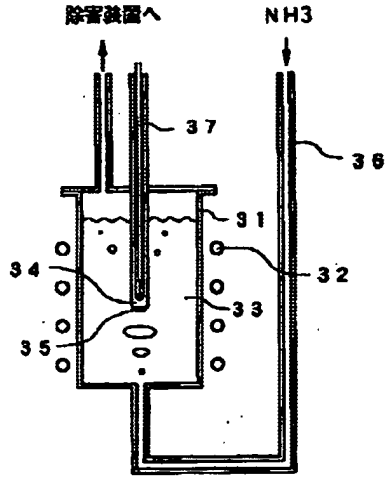
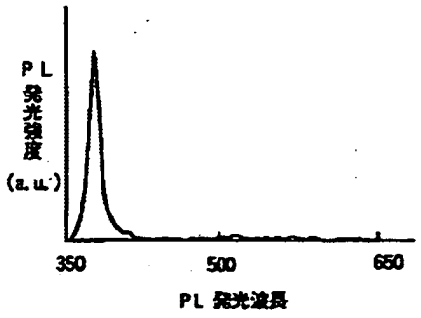
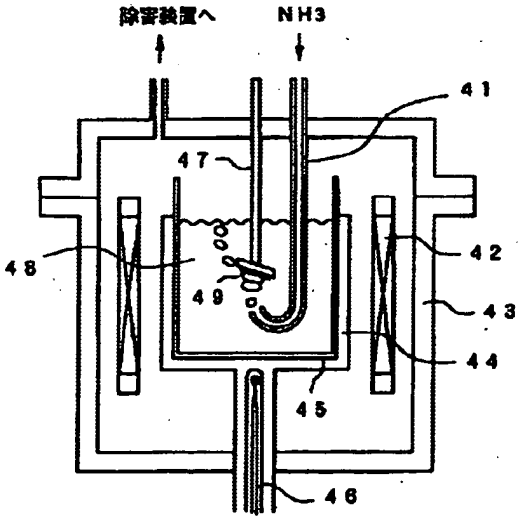


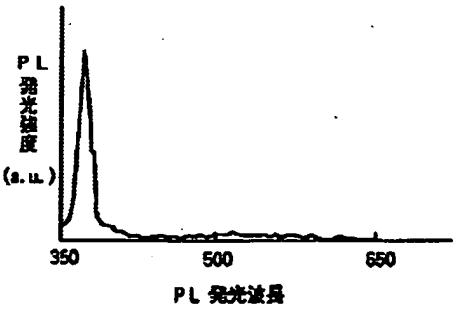
【図１０】



【図１１】



【図１２】



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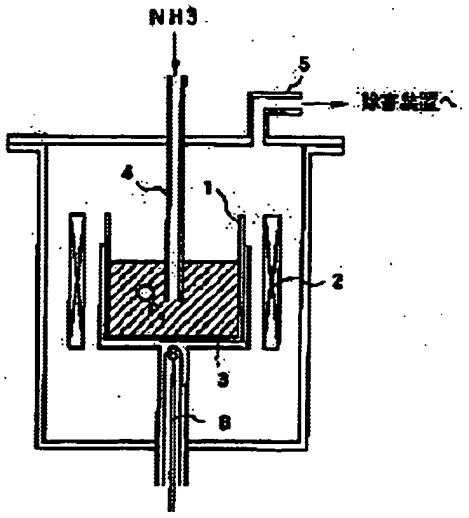
(54) PRODUCTION OF NITRIDE CRYSTAL, MIXTURE, LIQUID PHASE GROWTH, NITRIDE CRYSTAL, NITRIDE CRYSTAL POWDER, AND VAPOR GROWTH

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new method for crystal growth, enabling high-purity group III nitride crystal such as of GaN to be produced easily at low cost, in view of having been difficult to obtain large-sized crystal of such nitrides so far.

SOLUTION: This new method comprises the following processes: a group III metallic element is heated and melted, the resulting melt 3 is then injected with a nitrogen atom-contg. gas such as NH3 at a temperature not higher than the melting point of the aimed nitride to produce group III nitride crystallites with high wettability to the melt 3; the resultant mixture of the above crystallites and the melt is used as starting material for the liquid growth process, or group III nitride powder afforded by eliminating the group III metallic element from the above mixture is used as starting material for the vapor growth process; alternatively, a seed crystal or substrate crystal is immersed in a group III element melt such as of Ga, bubbles of a nitrogen- contg. gas such as NH3 are intermittently contacted with the surface of the above crystal to react the gas with the group III element on the surface to effect the growth of the aimed group III nitride crystal on the surface.



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CLAIMS

[Claim(s)]
[Claim 1] III It is III at the temperature below the melting point of the nitride which is going to heat a group metallic element, and is going to dissolve and it is going to obtain. The gas containing a nitrogen atom is poured into the melt of a group metallic element, and it is III. It is III within the melt of a group metallic element. The manufacture technique of the nitride crystal characterized by manufacturing a group's nitride microcrystal.
[Claim 2] It sets to the manufacture technique of a nitride crystal according to claim 1, and is III. III which doped this impurity element by mixing the impurity element with the group metallic element The manufacture technique of the nitride crystal characterized by manufacturing a group's nitride crystal.
[Claim 3] III obtained by the manufacture technique of a nitride crystal according to claim 1 or 2 A group's nitride microcrystal and III Mixture of a group metallic element.
[Claim 4] III obtained by the manufacture technique of a nitride crystal according to claim 1 or 2 A group's nitriding microcrystal and III III characterized by using the mixture of a group metallic element for a start raw material The liquid-phase-epitaxy technique of a group's nitride crystal.
[Claim 5] III obtained by the manufacture technique of a nitride crystal according to claim 1 or 2 A group's nitride microcrystal and III III obtained by the liquid-phase-epitaxy technique which used the mixture of a group metallic element for the start raw material A group's nitride crystal.
[Claim 6] III obtained by the manufacture technique of a nitride crystal according to claim 1 or 2 A group's nitride microcrystal and III The mixture of a group metallic element to III III which removes a group metallic element and is obtained A group's nitride crystal powder.
[Claim 7] III according to claim 6 III characterized by using a group's nitride crystal powder for a start raw material The vapor-growth technique of a group's nitride.
[Claim 8] III according to claim 6 III which used a group's nitride powder for the start raw material III obtained by the vapor-growth technique of a group nitride A group's nitride crystal.
[Claim 9] III according to claim 6 III characterized for a group's nitride crystal powder by melting, the re-freezing, or sintering The manufacture technique of a group's nitride crystal.
[Claim 10] III according to claim 6 a group's nitride crystal powder — melting — re—— III solidified, or sintered and obtained A group's nitride crystal.
[Claim 11] It sets to the manufacture technique of a nitride crystal according to claim 1 or 2, and is the above III. The manufacture technique of the nitride crystal characterized by for a group element being either among aluminum, Ga, and In, and the gas containing the above-mentioned nitrogen atom being ammonia gas.
[Claim 12] III heated and dissolved Seed crystal is immersed into a group element and it is III. By contacting intermittently the foam of the gas which contains a nitrogen atom on this seed crystal front face in a group element, it is III to this seed crystal front face. The manufacture technique of the nitride crystal characterized by growing up the nitride crystal of a group element.
[Claim 13] III heated and dissolved A substrate crystal is immersed into a group element and it is III. By contacting intermittently the foam of the gas which contains a nitrogen atom on this substrate crystal front face in a group element, it is III to this substrate crystal front face. The manufacture technique of the nitride crystal characterized by growing the nitride single crystal of

a group element epitaxially.
[Claim 14] It sets to the manufacture technique of a nitride crystal according to claim 12 or 13, and is the above III. The manufacture technique of the nitride crystal characterized by for group elements being aluminum, Ga, or the Ins, and the gas matter containing the aforementioned nitrogen atom being ammonia gas.
[Claim 15] It sets to the manufacture technique of a nitride crystal according to claim 12 or 13, and is the above III. The manufacture technique of the nitride crystal characterized by the temperature of a group element melt being lower than the melting point of the nitride crystal to grow up.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention is III. It is related with the manufacture technique, the mixture, the liquid-phase-epitaxy technique, the nitride crystal, the nitride crystal powder, and the vapor-growth technique of nitride crystals, such as a nitride crystal of a group element, especially GaN, AlN, InN.
[0002]
[Description of the Prior Art] It still cuts and is III with large-sized GaN, AlN, InN, etc. The method of manufacturing a group nitride crystal easily does not exist. If GaN bulk crystal is made, for implementation of a blue laser diode etc., the impact measures and will not be found. Moreover, it is thought that it will get into stride if the bulk crystal of a wide cap semiconductor material will enter in the 21st century.
[0003] As technique of manufacturing the crystal powder of GaN, it is Ga2 O3. The method of making the oxide of Ga of a grade react with ammonia, and manufacturing it is put in practical use, and the powder manufactured by this is marketed for reagents.
[0004] III The method of manufacturing the bulk crystal of a group nitride crystal easily is not yet developed. The size of the crystal whose manufactures of a crystal are risk and **** since a very high pressure is needed slightly, although the following reference is announced by S.Porowski et al. and which was obtained comparatively is about several millimeters and the parvus.
[0005] "Prospects for high-pressure crystal growth of III-V nitrides"S.porowski, J.Jun, P.Perlin, I.Grzegory, H.Teisseyre and T.Suskilnst.Phys.Conf.Ser.No.137 : Chapter III represented by 4Paper presented at the 5th SiC and Related Materials Conf., Washington and DC, and 1993GaN A group nitride The melting point is very high, and since sublimation and decomposition happen at the temperature below the melting point, the melt cannot be made and the crystal growth from a melt is not made. Moreover, III Since the solubility to a group melt is very low, the crystal growth from a solution is also difficult. III put in practical use until now The crystal-growth technique of a group nitride is only three sorts of vapor-phase-epitaxial-growth methods, HVPE (hydride vapor growth), the MOVPE (organic-metal vapor growth) method, and the MBE (molecular beam epitaxy) method. Light Emitting Diode of GaN system manufactured by this has come [moreover,] to be marketed. The following reference is announced as an example of the crystal growth of GaN by the MOVPE method.
[0006] "Novel metalorganic chemical vapor deposition system for GaN growth" S.Nakamura, Y.Harada and M.Seno, Appl.Phys.Lett.58 (18) 6, 1991 [0007]
[Problem(s) to be Solved by the Invention] III represented by GaN The nitride crystal of a group element attracts attention as a material for blue light emitting devices in recent years. In order to create an element, it is necessary to grow for example, GaN crystal etc. epitaxially on a substrate. In this epitaxial growth, in order to prevent the occurrence of asymmetry under crystal which grows, it is ****-like that the lattice constant and coefficient of thermal expansion of the crystal used as a substrate are the same as that of the crystal which grows on it. However, so far, as a substrate, the bulk crystal of the nitride which can be used was not

obtained, but the silicon on sapphire from which a lattice constant is different reluctantly was substituted for it, and it has grown epitaxially on it.

[0008] As an epitaxial grown method, although the present MOVPE method is in use, it is easy to ignite, and the organic metal of a raw material is dangerous, and be expensive. Furthermore, need large-scale, complicated, and expensive growth equipment. It is not avoided that hydrogen enters as an impurity, but this becomes a cause, and problems, like a raise in the carrier of p type crystal is difficult are during a growth crystal.

[0009] Therefore, in order to form p type crystal into a high carrier, it is necessary to bring p type dielectric layer to an element front face, and to perform nitride crystal processing. Since there was the need of bringing p type dielectric layer to an element front face, the degree of freedom of a design of element structure was narrow.

[0010] As other epitaxial grown methods, it is III. It is III to the solvent of a group element. There is a method of melting and carrying out LPE (liquid phase epitaxial) growth of the group nitride crystal as a solute. However, III marketed conventionally A group nitride crystal is Ga2 O3, if it is GaN. It was the impalpable powder which the oxide of Ga of a grade was made to react with ammonia, and manufactured it, and it originated in the configuration, and the front face of GaN crystal seldom got wet with Ga, therefore there was a problem are hard to solve in Ga.

[0011] An application is expected also as a dopant material [in / as a fluorescence material / liquid phase epitaxial growths, such as GaAs and GaP, in the fine particles of a nitride crystal]. However, GaN crystal powder marketed conventionally was unsuitable for the expensive start raw material that purity is comparatively low and for vapor growths. Moreover, since it originated in the configuration and it was hard to solve in a semiconductor melt, there was a problem are hard to use also as the raw material and dopant raw material for liquid phase epitaxies.

[0012] The trouble of the above conventional techniques is canceled and the purpose of this invention is high grade GaN III. It is in the thing which can obtain the nitride crystal of a group element easily and cheaply and for which the manufacture technique, the mixture, the vapor-growth technique, the nitride crystal, the nitride crystal powder, and the vapor-growth technique of a new nitride crystal are proposed.

[0013] Moreover, other purposes of this invention are IIIs, such as GaN which was not obtained until now. It is [the new crystal-growth technique that the bulk crystal of the nitride crystal of a group element can be grown up easily, and] III simple and safely. It is in proposing the new crystal-growth technique which can grow a group nitride crystal epitaxially.

[0014]

[Means for Solving the Problem] The 1st main point of this invention is roughly divided, and there are three.

[0015] ** They are IIIs, such as hot Ga, about the gas containing nitrogen, such as ammonia. It is made to react by pouring into the melt of a group element. Thereby, it is III. It is III in the melt of a group element. The microcrystal of a group nitride floats in large quantities.

[0016] ** III obtained in this way A group element and III Mixture of a group nitride microcrystal is used as a raw material, and it is III. The liquid phase epitaxial growth of a group nitride crystal is performed. III obtained by above-mentioned technique a group element nitride microcrystal — III the concordance with a group element melt — good — III a group nitride microcrystal — III it melts in a group element melt easily — making — **** — things are made

[0017] ** It is III at the above-mentioned mixture to an acid cleaning etc. III which removes a group element and is obtained A group nitride microcrystal is used as a raw material, and it is III. The vapor growth of a group nitride crystal, synchysis, and a sintering crystal are manufactured. The raw material obtained by this technique has a high grade and the characteristic feature of being cheap.

[0018] It is III for explaining in full detail. The technique of pouring the steam of V group element into a group melt, and compounding an III-V group compound is called injection (injection) method, and is well-known technique. For example, there are also the following society reports as an example which compounded the polycrystal of InP which is one of the III-V group compound semiconductors.

[0019] the 34th besides "extensive synthesis of InP polycrystal by the P-injection method", and

Shibata — time applied physics relation union lecture meeting (1987) 28p-Z-1, however injection A method III Heat beyond the melting point of the III-V group compound which compounds a group melt, and the steam of V group element is poured in there. As opposed to being one of the so-called melt grown methods which make the melt of an III-V group compound, once cool this, and produce a crystal to the claim 1 of this invention the synthesis method of such a nitride It is III at temperature much lower than the melting point of the nitride to compound. The gas containing nitrogen is poured in into a group melt. III of the liquid phase A group element and V group element of a gaseous phase are made to react, and it is III. It is III of solid phase in a group element melt. The conventional injection in the point of generating a group nitride crystal directly (the melt of a nitride not being made) A method is a completely different new synthesis method. This is III of a nitride. The characteristic feature that the solubility to a group element melt is very low is taken to a foul trick, and is used positively.

[0020] It sets to the manufacture technique of this nitride crystal according to claim 1, and is III. III which doped the impurity by mixing the impurity element with the group metallic element A group's nitride crystal can be manufactured (claim 2). And by the manufacture technique of this nitride crystal according to claim 1 or 2, it is III. A group's nitride powder and III The mixture of a group metal raw material is obtained (claim 3).

[0021] It is such III to the claim 4 of this invention. A group nitride crystal and III The mixture of a group metal raw material is III. Although a group nitride crystal is a microcrystal, the front face is completely III. The big characteristic feature is in the point of having got wet from the group metal raw material. In case a crystal impalpable powder is added to a dopant, it compares with the volume, and the big mark powder of a surface area is [the raw material for liquid phase epitaxies, and] III. There is a problem are very hard to melt that it is [therefore] hard to get used to a group melt. Especially, in the nitride crystal with low saturation solubility, this difficulty of melting serves as a fatal fault for a crystal growth. III which is marketed conventionally Most group nitrides are in the impalpable-powder status, and had the above-mentioned fault uniformly. It is such III to this invention. Group nitride microcrystal powder and III For the mixture of a group metal raw material, a nitride crystal is III. Since it is compounded in a group melt, the front face is completely III. When it is covered from the group metal raw material and it uses as a liquid-phase-epitaxy raw material, it is very easy to melt, and can be easily reached and made saturation solubility compared with the conventional raw material. Consequently, the controllability of epitaxial growth and repeatability improve by leaps and bounds, and it is high grade III. A group's nitride crystal is obtained (claim 5).

[0022] Moreover, the conventional III At a group nitride synthesis method, it is III to a raw material. In order to use a group's oxide and chloride, the process which removes an unreacted object from the compound nitride powder was surely required. It is III, in case an unreacted object does not turn into the impurity at the time of a liquid phase epitaxy, therefore it uses for the raw material of a liquid phase epitaxy, since neither the oxide nor the chloride is used for the raw material by such manufacture technique at the claims 1, 2, and 4 of this invention. Let this mixture be the raw material of a direct liquid phase epitaxy, without extracting only a group nitride. It not only leads to large compaction of a process, but that this extraction process is omissible can lose contamination of the raw material which tends to be generated at an extraction process, and the high grade liquid phase epitaxy of it becomes possible.

[0023] this invention is applicable also to the vapor-growth technique although invention given in the above-mentioned claims 3-5 relates to the liquid-phase-epitaxy technique. That is, invention according to claim 6 is III obtained by the manufacture technique of a nitride crystal according to claim 1 or 2. A group's nitride microcrystal and III The mixture of a group metal raw material to III III which removes a group metal raw material and is obtained It is a group's nitride crystal powder. This nitride crystal powder is used for a start raw material, and it is III. It is III by the vapor growth to which the vapor growth of a group's nitride crystal can be carried out (claim 7). A group's nitride crystal can be obtained (claim 8).

[0024] Moreover, invention according to claim 9 is III according to claim 6. About a group's nitride powder, they are melting, the re-freezing, or III to sinter. It is III from which it is the manufacture technique of a group's nitride crystal, and invention according to claim 10 was obtained by the

manufacture technique. It is a group's nitride crystal.
[0025] In addition, it sets to the manufacture technique of a nitride crystal according to claim 1 or 2, and is the above III. Also let the gas which a group element is either among aluminum, Ga, and In, and contains the above-mentioned nitrogen atom be ammonia gas (claim 11). Furthermore, it also sets to invention according to claim 3 to 10, and is III. Let a group element be either among aluminum, Ga, and In.
[0026] The 2nd main point of this invention is IIIs, such as a gallium. Seed crystal or a substrate crystal is immersed into the melt of a group element, the foam of the gas which contains nitrogen, such as ammonia, on the front face is contacted intermittently, and it is III in the front face of seed crystal or a substrate crystal. By making the gas containing a group element and nitrogen react, it is III to the front face. It is the technique of growing up the nitride crystal of a group element.
[0027] It is III at temperature much lower than the melting point of the nitride which also compounds this nitride crystal-growth method. The gas containing nitrogen is poured in into a group melt, and it is III of the liquid phase. A group element and V group element of a gaseous phase are made to react, and it is III. It is III of solid phase in a group element melt. It is premised on generating a group nitride crystal directly (the melt of a nitride not being made). This is III of a nitride. As the characteristic feature that the solubility to a group element melt is very low is taken to a foul trick, it uses positively and this premise itself already stated, it is the above-mentioned injection. A melt grown method like a method is a crystal-growth method based on the completely different new idea.
[0028] IIIs, such as a gallium, aluminum, and an indium If compared with the melting point (for example, called 2000 degrees C or more if it is GaN) of a nitride, it will react at the quite low temperature of about several 100-1000 degrees C, and the gas containing a group element and nitrogen, such as ammonia and a hydrazine, is III. Generating a group nitride is known. For example, there are the following reports.
[0029] "Crystal growth of GaN by reaction between Ga and NH 3" D.E1well et.al. and J.Crystal Growth 66 (1984) 45-54, however generated GaN are III. It does not melt in a group melt, but it becomes an impalpable powder, and is III. It only separates on the front face of a group melt.
[0030] By the manufacture technique of a nitride crystal according to claim 12 or 13, they are IIIs, such as a gallium. Seed crystal or a substrate crystal is immersed into the melt of a group element, and the foam of the gas which contains nitrogen, such as ammonia, on the front face is contacted intermittently. It is III in the front face of seed crystal or a substrate crystal. III combined with the front face of seed crystal or a substrate crystal by making the gas containing a group element and nitrogen react A group atom can be nitrided and a nitride crystal can be grown up to a substratum. If this reaction is performed continuously, growth of an epitaxial film and bulk crystal growth can be performed.
[0031] In addition, also let the gas which the above-mentioned III group element is either among aluminum, Ga, and In, and contains the above-mentioned nitrogen atom be ammonia gas in the manufacture technique of a nitride crystal according to claim 12 or 13 (claim 14). Furthermore, it sets to the manufacture technique of a nitride crystal according to claim 12 or 13, and is the above III. Temperature of a group element melt is made lower than the melting point of the nitride crystal to grow up (claim 15).
[0032]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained focusing on an example.
[0033] (Example 1) The equipment which is shown in drawing 1 was manufactured as one example of this invention. The example which compounded GaN microcrystal is described using this equipment.
[0034] 3000g of Gas was held in the with a bore height [150mm height of 70mm] quartz crucible 1, Ga was heated to 950 degrees C at the heater 2, and the Ga melt 3 was formed. Then, the gas introduction piping 4 is used and it is 0.51/min about ammonia gas in the Ga melt 3. It continued blowing in by the flow rate for 5 hours. The gas blown into the melt 3 reacted with the melt, and generated GaN microcrystal, and the microcrystal emerged on the melt front face. The ammonia

gas which was not contributed to a reaction serves as foam, passes through the inside of a melt 3, comes out to the space of the container upper part, and is discharged out of a container through an exhaust pipe 5. The discharged ammonia gas was emitted to the atmospheric air through wet damage elimination equipment. After performing insufflation of 5 hours, the gas to pour in was changed to nitrogen and Ga melt was cooled to the room temperature.

[0035] When cooled Ga melt was taken out from the container and observed, the microcrystal of GaN was appearing on the upper part of Ga melt in large quantities. The front face of GaN microcrystal was in the status which got wet with Ga melt completely. As for Ga melt, the 10.2g increase in a weight accepted before and after synthetic work. When calculated from here, 61g GaN microcrystal is able to be compounded.

[0036] (Example 2) It carried out like an example 1, GaN microcrystal was compounded, the mixture of Ga melt which appears on the upper part of Ga melt, and GaN microcrystal was used for the raw material, and the liquid phase epitaxial growth of GaN was performed by the slide boat method. The cross section of the equipment used for growth is shown in drawing 2 . Ga melt and 20g of the mixture of GaN mark crystal were put into the graphite boat 11 as a raw material 12. The c-th page silicon on sapphire 16 of 25mm angle was set to the slide boat 17. The inside of the quartz coil 14 was made into the nitrogen gas draft ambient atmosphere, and the raw material was heated until thermocouple 15 output became 1150 degrees C at the heater 13. After leaving it in this status for 4 hours, temperature was lowered to 1100 degrees C, the joy stick 18 was lengthened, the slide boat 17 was moved, and silicon on sapphire 16 was contacted in the raw material 12. this or subsequent ones — raw material temperature — 1 degree C/m — comparatively — coming out — up to [600 degrees C] — lowering — a joy stick 18 — pushing — the slide boat 17 — the original position — returning — a substrate 16 and the raw material 12 — separation — the bottom Heater power was turned off after that and it cooled to the room temperature. The temperature program at the time of a liquid phase epitaxial growth is shown in drawing 3 .

[0037] The substrate which growth finished was taken out and the front face and the cross section were observed. The transparent layer was growing on the surface of silicon on sapphire. The thickness for which it asked from SEM observation of a cross section was 4.2 micrometers. The photoluminescence measurement result in the room temperature of the grown-up layer is shown in drawing 4 . The 360nm sharp photogenesis peak corresponding to band edge photogenesis of GaN is observed, and it checked that the grown-up layer was a good GaN layer. When the electrical property of the grown-up layer was measured by the fan ******** (Van der Pauw) method, carrier concentration is 1x1017cm-3 and mobility is 520cm2 / V, and sec. The good property was shown.

[0038] (Example 3) By the same technique as an example 1, 20mg Si was beforehand put into the raw material Ga, GaN microcrystal was compounded, the mixture of obtained Ga melt and GaN microcrystal was used for the raw material, and liquid phase ********** growth of GaN was performed by the same slide boat method as an example 2.

[0039] The photoluminescence measurement result in the room temperature of obtained GaN layer is shown in drawing 5 . The 369nm sharp photogenesis peak corresponding to photogenesis of the Si dope GaN is observed, and it checked that Si was doped by the grown-up layer. When the carrier concentration of the grown-up layer was measured by the fan ******** method, it was n type 6x1018cm-3.

[0040] (Example 4) By the same technique as an example 1, 7mg Mg was beforehand put into the raw material Ga, GaN microcrystal was compounded, the mixture of obtained Ga melt and GaN microcrystal was used for the raw material, and the liquid phase epitaxial growth of GaN was performed by the same slide boat method as an example 2.

[0041] The photoluminescence measurement result in the room temperature of obtained GaN layer is shown in drawing 6 . The 445nm photogenesis peak corresponding to photogenesis of the Mg dope GaN is observed, and it checked that Mg was doped by the grown-up layer. When the carrier concentration of the grown-up layer was measured by the fan ******** method, it was p type 5x1017cm-3. If the layer obtained by MOVPE growth does not add heat treatment, Mg under crystal is not activated, but the Mg dope GaN layer obtained by this technique showed the

good p type electrical property in the state of ********** to p type electrical property not being shown. This is considered because there was no mixing of the hydrogen atom which bars an activation of Mg.

[0042] (Example 5) After having extracted the undoping GaN microcrystal compounded by the same technique as an example 1, and the mixture of a metal Ga, having added a hydrochloric acid and hydrogen peroxide solution to this and melting only Ga, it **ed through the filter paper and only GaN mark crystal was taken out. After the pure water fully washed the filtered powder, it was dried within the vacuum thermostat. Consequently, 61g of the powder which carried out off-white was obtained. When this powder was observed under the microscope, it consisted of a microcrystal based on six[about / particle-size -10micrometer] -sided prisms. The room temperature photoluminescence measurement result of this powder is shown in drawing 7 . The 360nm sharp photogenesis peak corresponding to band edge photogenesis of GaN is observed, and the obtained mark crystal checked that it was good GaN. Although the concentration of the impurity which may be mixed into the obtained powder was investigated by the secondary ion mass spectrometry (SIMS), except that Si considered to be mixing from a quartz container was detected about [5x1015cm -] three, it was below limit of detection altogether.

[0043] (Example 6) GaN microcrystal powder obtained in the example 5 was used for the raw material, and the equipment which is shown in drawing 8 performed the vapor phase epitaxial growth of GaN. As a raw material, 25g of GaN microcrystal powder 26 was put into the quartz crucible 23 with a diameter of 50mm, and it set to it in the quartz container 21 in support of this by the graphite susceptor 25. On the other hand, the c-th page silicon on sapphire 28 of 25mm angle was fixed to the substrate electrode holder 22 made from graphite, and the substrate was hung in the quartz crucible 23 so that a substrate front face might counter with a raw material 26. The inside of the quartz container 21 was replaced by the ammonia gas ambient atmosphere in this status, and the raw material was continuously heated for ammonia gas at the heater 24 with the 0.5l./m sink. Heating is the output of the thermocouple 27 arranged on the bottom of a crucible, and was controlled to become 1100 degrees C. At this time, the skin temperature of a substrate 28 had become about 850 degrees C. The crystal growth was performed by holding for 24 hours and making it sublimate, where a raw material is heated.

[0044] The transparent layer of GaN had grown to be the front face of the taken-out silicon on sapphire. When the front face of GaN layer was observed under the microscope, mol ******** which carried out the trigonum - the hexagonal method was observed. The mean thickness of the grown-up layer was about 400 micrometers. When the electrical property of the grown-up layer was measured by the fan ******** method, carrier concentration 2x1017cm-3 and mobility are 490cm2 / V, and sec. The good property was shown.

[0045] (Example 7) By the same technique as an example 1, In was used instead of Ga and InN was compounded. Except having made synthetic temperature into 600 degrees C, they are the same conditions as an example 1. Before it cooled In which synthesis finished to 180 degrees C and In solidified, the mixture of InN microcrystal and the metal In which appeared on the upper part of In melt was taken out.

[0046] After having added a hydrochloric acid and hydrogen peroxide solution to this mixture and melting only In, it **ed through the filter paper and only InN microcrystal was taken out. After the pure water fully washed the filtered powder, it was dried within the vacuum thermostat. Consequently, it was obtained about 200g of the powder which carried out thin off-white. When this powder was observed under the microscope, it consisted of a microcrystal based on a six [about / particle-size -8micrometer] -sided prism. When the ********** spectrum of the obtained powder was measured, the 650nm photogenesis equivalent to band edge photogenesis of InN was observed.

[0047] (Modification) Focusing on the crystal growth of GaN, the above-mentioned example described the crystal growth of InN further, and it is applicable also to crystal growths, such as AlN, and AlGaN which is the mixed crystal of AlN or InN, GaInN.

[0048] As gas containing nitrogen, the use of a hydrazine, a monomethylhydrazine, etc. other than ammonia can be considered.

[0049] Although the example of a liquid phase epitaxy was described about the crystal growth

under atmospheric pressure, if it carries out under the hyperbaric pressure of nitrogen or the ammonia ambient atmosphere, a rate of crystal growth can be gathered further.
[0050] Although the example of a liquid phase epitaxy and a vapor growth was described about epitaxial growth of a up to [silicon on sapphire], the application expansion to the bulk crystal growth of a nitride is also possible to the epitaxial growth using other substrates, and the pan.
[0051] The yield and particle size of a nitride microcrystal which are obtained by synthesis are III. It is possible to control by residence time of gas, such as ammonia poured in into the group melt. Therefore, the nose of cam configuration of the filling pipe of gas can be changed, or a modification, such as preparing into a melt the path along which the foam of gas passes by quartz work etc., can be considered.
[0052] (others — operation gestalt) the nitride microcrystal obtained by this invention is widely [as a semiconductor material or a fluorescent substance material] applicable If especially liquid-phase-epitaxy technique [such] is applied to a manufacture of the light emitting device of ultraviolet - yellow, it is effective for one of this inventions.
[0053] For example, if two raw material stowages are established in the liquid-phase-epitaxy equipment stated in the example 2, a Mg dope GaN raw material is held in one side and an Si dope GaN raw material is held in another side, GaN layer of p type and n type can be continuously grown up on a substrate. In this way, if Light Emitting Diode manufacture process is given to the obtained epitaxial growth substrate, pn junction type blue Light Emitting Diode can be manufactured easily. According to this technique, Light Emitting Diode can be manufactured simply and safely, and more cheaply than the conventional MOVPE method. Moreover, in the conventional MOVPE method growth GaN, in order to produce p type crystal, heat treatment needed to be added afterwards, and there was constraint that element structure had to be designed so that a crystal front face may always become p type for this reason. Since it will be obtained even if p type conductivity does not heat-treat if such a liquid phase epitaxy is used for this invention, the tolerance of the mechanical design of an element becomes very large.
[0054] In addition, since the amount of the synthetic temperature of a nitride, the ambient-pressure force, and the raw material used etc. changes with the modality of nitride to compound, or modalities of raw material to use, it is difficult the amount etc. to decide the optimum conditions uniquely.
[0055] (Example 8) The equipment which is shown in drawing 9 was manufactured as an example of the octavus of this invention. The example which performed GaN crystal growth is described using this equipment.
[0056] 3000g of Gas33 dissolved in the with a bore height [200mm height of 70mm] quartz container 31 was held, and during melting Ga33, it was attached at the nose of cam of the seed crystal support fixture 34, having used the fragment of 6mm one side SiC single crystal as seed crystal 35, and it fixed. Melting Ga33 was heated at the heater 32, and it controlled by this status to become 1000 degrees C with the output of a thermocouple 37.
[0057] Then, introducing ammonia gas at a rate of 0.2l./m from the base of a quartz container for 76 hours was continued through the ammonia introduction spool made from a quartz 36 with a bore of 6mm. The ammonia gas introduced during melting Ga33 became the foam, and started the inside of a melt. The number of foam was about 350 per minute. The foam of ammonia gas which goes up the inside of a melt collides with the front face of seed crystal 35, and generates GaN crystal one after another on the seed crystal front face. As it is, as foam, unreacted ammonia gas is attained to a melting Ga front face, and is discharged out of a container. The discharged gas eliminated the damage and carried out atmospheric-air exudation by wet **********. Also except the front face of seed crystal, the foam of ammonia gas reacted with Ga and generated GaN. This GaN was a microcrystal with a diameter of micrometers [about several], came floating to the melting Ga front face, and did not contribute to growth on seed crystal.
[0058] The crystal which growth finished was cooled, it took out out of melting Ga, and the metal Ga adhering to the front face was washed out with the hydrochloric acid. Consequently, GaN crystal of the shape of a with a diameter height [about 6mm height of about 10mm] hexagonal prism was obtained on the seed crystal of SiC. The obtained crystal was presenting a

transparent yellowish brown color. The obtained crystal checked that it was GaN crystal with the X-ray diffraction method. an X-ray diffraction full width at half maximum (FWHM) — about 2 mins it is — it can be said that the obtained crystal has good crystallinity

[0059] The photoluminescence measurement result in the room temperature of the obtained crystal is shown in drawing 10 . The sharp photogenesis peak corresponding to band edge photogenesis of undoping GaN is observed by 360nm, and it has checked to it, that it was good GaN crystal also by photoluminescence measurement.

[0060] (Example 9) The equipment which is shown in drawing 11 was manufactured as the 9th example of this invention. The example which grew GaN crystal epitaxially is described using this equipment.

[0061] The with a bore height [150mm height of 70mm] quartz crucible 45 was put into the graphite susceptor 44, and it installed in the interior of the stainless steel container 43. 3000g of dissolved Gas48 was held in the interior of the quartz crucible 45, and during melting Ga48, the 25mm one side c-th page sapphire single crystal substrate (henceforth silicon on sapphire) 49 was attached at the nose of cam of the substrate support fixture 47, and it was immersed. In melting Ga, since silicon on sapphire 49 was level about several degrees, it leaned and it was fixed. Moreover, during melting Ga48, the ammonia gas introduction spool 41 made from a quartz which bent the nose of cam to the J character type was installed. The nose of cam of the gas introduction spool 41 was fixed so that it might become directly under the edge of the lower one of silicon on sapphire 49. Melting Ga48 was heated at the heater 42, and it controlled by this status to become 950 degrees C with the output of a thermocouple 46. Then, ammonia gas was introduced at a rate of 0.1l./m during melting Ga48 through the ammonia introduction spool 41 for 1 hour. The introduced ammonia gas became the foam and started the inside of a melt. The number of foam was about 200 per minute. After the foam of ammonia gas which went up the inside of a melt collided with the soffit of silicon on sapphire 49 and went up along the substrate front face, it reaches up to melting Ga48 front face, and was discharged out of the container. The discharged gas eliminated the damage and carried out atmospheric-air exudation by wet **********.

[0062] The crystal which growth finished was cooled, it took out out of melting Ga48, and the metal Ga adhering to the front face was washed out with the hydrochloric acid. Consequently, the transparent crystal thin film with a thickness of about 4 micrometers was obtained on silicon-on-sapphire 49 front face. The obtained crystal checked that it was GaN crystal with the X-ray diffraction method. an X-ray diffraction full width at half maximum (FWHM) — about 5 mins it was .

[0063] Photoluminescence ****** in the room temperature of the obtained crystal is shown in drawing 12 . The sharp photogenesis peak corresponding to band edge photogenesis of undoping GaN is observed by 360nm, and it has checked to it, that it was good GaN crystal.

[0064] In addition, since it changes with the modality of nitride which grows, or modalities of raw material to use, nitride crystal-growth temperature, the ambient-pressure force under growth, the amount of the raw material used, etc. are not decided uniquely.

[0065] Although it is for according to the result which activity chooses ammonia to some extent chemically, and took safety and economical efficiency into consideration as gas containing nitrogen, gas, such as a hydrazine and a monomethylhydrazine, can also be used theoretically. However, these gas has the far large risk of an explosion compared with ammonia.

[0066] III in a crystal growth Group raw material temperature was made below into the melting point of the nitride which grows for preventing the grown-up crystal's decomposing or carrying out a remelting solution.

[0067] (Modification) At an example, it is GaN. It is applicable also to crystal growths, such as InN, AlN and AlGaN that are such mixed crystal, and GaInN, although the crystal growth was described. Furthermore, III The nitride crystal which doped the impurity can also grow by mixing an impurity element into the gas containing the inside of a group melt, or nitrogen.

[0068] As gas containing nitrogen, the use of a hydrazine, a monomethylhydrazine, etc. other than ammonia can be considered.

[0069] III The nose of cam configuration of the spool which introduces gas, such as ammonia,

into a group melt is the purpose which controls the large number of **s of the foam of the gas in a melt, and can consider deformation variously. For example, two or more diffusers of the foam can be prepared at the nose of cam of a gas introduction spool, or a network can be formed at the nose of cam of a gas introduction spool.

[0070] III The modification which installs two or more seed crystal and substrate crystals into a group melt is also considered.

[0071] Although the example shown in above-mentioned view 1 , the drawing 2 , the drawing 8 , the drawing 9 , and the drawing 11 described only the crystal-growth container in which the main point fraction of this invention is shown, if the system which combined the thermoregulator which can carry out program control of the temperature of the mass-flow controller which adjusts a quantity of gas flow, or a heater automatically as a peripheral device of growth equipment is built, a control of a crystal growth will become easy more.

[0072] The nitride crystal obtained by this invention is widely [as a semiconductor material or a fluorescent substance material] applicable. Especially the bulk single crystal substrate of a nitride is the optimum as a substrate material at the time of manufacturing blue laser diode.

[0073]

[Effect of the Invention] As explained above, according to this invention, the following outstanding effects are acquired.

[0074] (1) It is III at the temperature much lower than the melting point of the nitride to compound according to the manufacture technique according to claim 1 to 2. The gas containing nitrogen is poured in into a group melt. III of the liquid phase A group element and V group element of a gaseous phase are made to react, and it is III. It is III of solid phase in a group element melt. Since a group nitride crystal is generated directly, compared with the case where the melt of a nitride is made, it can manufacture in large quantities to the inside of a short time cheaply easily with easy equipment.

[0075] (2) It is such III to the claim 3 of this invention. A group nitride microcrystal and III For the mixture of a group metal raw material, a nitride microcrystal is III. Since it is compounded in a group melt, the front face is completely III. If it is covered from the group metal raw material and this mixture is used for a liquid-phase-epitaxy raw material, it can very be easy to melt and the solution of saturation solubility can be easily obtained compared with the conventional raw material. Consequently, the controllability of epitaxial growth and repeatability improve by leaps and bounds.

[0076] (3) According to such growth technique to the claims 4, 7, and 9 of this invention, it is III. A group's high-grade nitride semiconducting crystal can be easily manufactured in large quantities to the inside of a short time cheaply with easy equipment. Moreover, it is not necessary to use dangerous raw materials, such as gas, such as chlorine conventionally used by the HVPE method, and an organic metal currently used by the MOVPE method, and is safe. Moreover, according to the growth technique of this invention, the liquid phase epitaxy and vapor growth of the conventionally difficult nitride crystal come be made especially easily. Consequently, a manufacture of the device which has p type crystal of a high carrier even if it does not give **** special to a nitride crystal becomes easy, and since the need of bringing p type electric conduction layer to an element front face is lost, the degree of freedom of a design of element structure spreads.

[0077] (4) Moreover, it is III, in case an unreacted object does not turn into the impurity at the time of a liquid phase epitaxy, therefore it uses for the raw material of a liquid phase epitaxy, since the oxide or chloride like before are not used for a raw material by the growth technique of such a nitride at the claims 4, 7, and 9 of this invention. Let this mixture be the raw material of a direct liquid phase epitaxy, without extracting only a group nitride. It not only leads to large compaction of a process, but that this extraction process is omissible can lose contamination of the raw material which tends to be generated at an extraction process, and the high grade liquid phase epitaxy of it becomes possible.

[0078] (5) Further according to such manufacture technique to the claims 12 and 13 of this invention, it is III. Growth of a group's nitride semiconducting crystal, especially the bulk single crystal which was not able to be grown up conventionally is attained. If this crystal is used for a

substrate, utilization of blue LD which has not yet resulted in utilization will be promoted upwards it is not only effective in efficient-izing and reinforcement of blue Light Emitting Diode, but, and it will contribute greatly. Moreover, such III A group's nitride semiconducting crystal can be grown up easily and cheaply with easy equipment. In addition, it is not necessary to use dangerous raw materials, such as gas, such as chlorine conventionally used by the HVPE method, and an organic metal currently used by the MOVPE method, and is safe.

[Translation done.]

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3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section of such GaN crystal-cultivation equipment at the 1st of this invention, and the 7th example.
[Drawing 2] It is the cross section of the liquid-phase-epitaxy equipment of such a GaN crystal at the 2nd example of this invention.
[Drawing 3] It is the graph which shows the temperature program at the time of the liquid phase epitaxy of such a GaN crystal to the 2nd example of this invention.
[Drawing 4] It is drawing showing the photoluminescence measurement result in the room temperature of such a liquid-phase-epitaxial-growth undoping GaN conjunctiva in the 2nd example of this invention.
[Drawing 5] It is drawing showing the photoluminescence measurement result in the room temperature of such a liquid-phase-epitaxial-growth Si dope GaN crystal layer in the 3rd example of this invention.
[Drawing 6] It is drawing showing the photoluminescence measurement result in the room temperature of such a liquid-phase-epitaxial-growth Mg dope GaN crystal layer in the 4th example of this invention.
[Drawing 7] It is drawing showing the photoluminescence measurement result in the room temperature of such undoping GaN microcrystal powder in the 5th example of this invention.
[Drawing 8] It is the cross section of the vapor-growth equipment of such a GaN crystal at the 6th example of this invention.
[Drawing 9] It is the cross section of such GaN crystal-growth equipment at the example of the octavus of this invention.
[Drawing 10] It is drawing having shown the photoluminescence measurement result in the room temperature of GaN crystal produced in the example of the octavus of this invention.
[Drawing 11] It is the cross section of such a GaN crystal epitaxial growth system at the 9th example of this invention.
[Drawing 12] It is drawing having shown the photoluminescence measurement result in the room temperature of GaN epitaxial growth crystal produced in the 9th example of this invention.
[Description of Notations]
1 Quartz Crucible
2 Heater
3 Ga Melt
4 Ammonia Insufflation Spool
5 Exhaust Pipe
6 Thermocouple
11 Graphite Boat
12 GaN Impalpable Powder and Mixture of Ga
13 Heater
14 Quartz Coil
15 Thermocouple
16 Silicon on Sapphire

17 Slide Boat made from Graphite
18 Joy Stick made from Quartz
21 Quartz Container
22 Substrate Electrode Holder made from Graphite
23 Quartz Crucible
24 Heater
25 Susceptor made from Graphite
26 GaN Microcrystal Powder
27 Thermocouple
28 Silicon on Sapphire
31 Quartz Container
32 Heater
33 Melting Ga
34 Seed Crystal Support Fixture
35 Seed Crystal
36 Ammonia Introduction Spool
37 With [Thermoelectricity]

[Translation done.]

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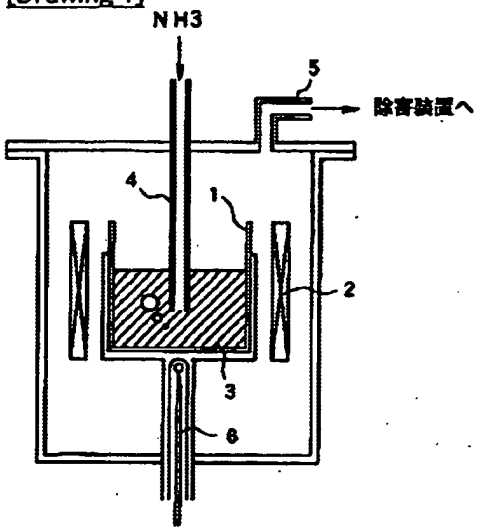
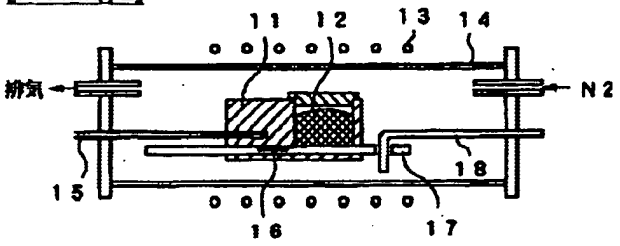
DRAWINGS

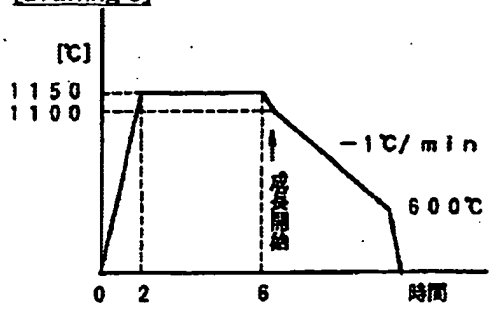
[Drawing 1]



[Drawing 2]



[Drawing 3]



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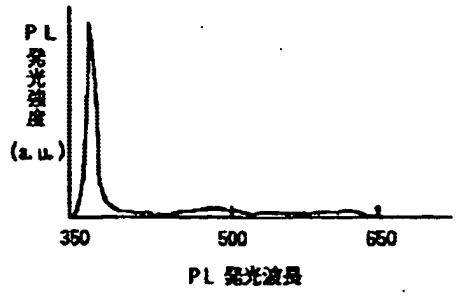
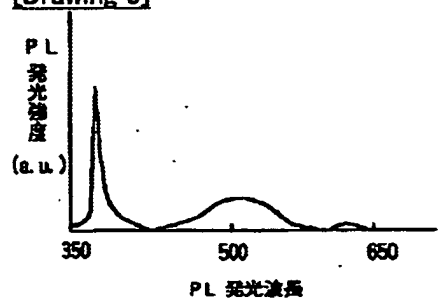


[Drawing 5]



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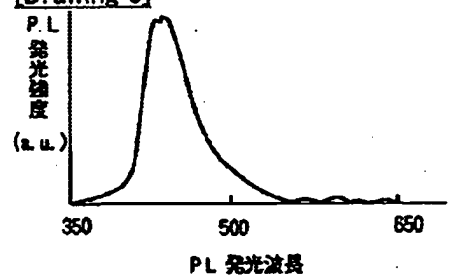

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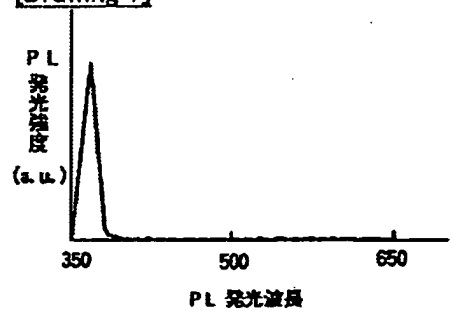
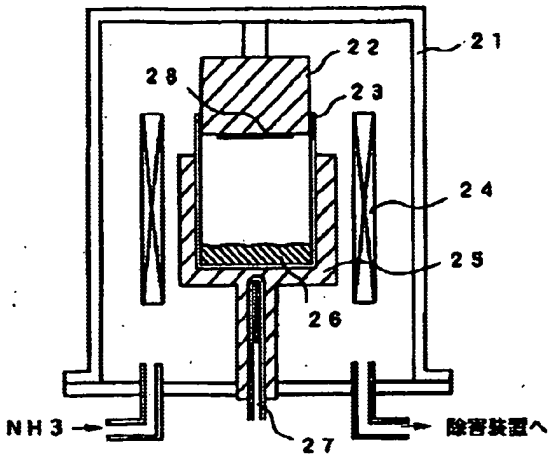
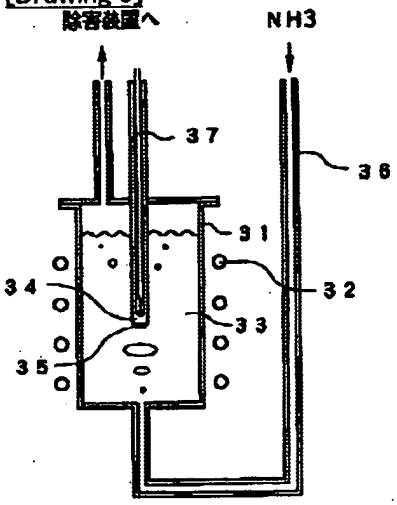


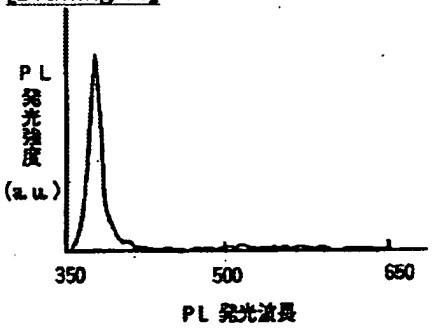
[Drawing 8]



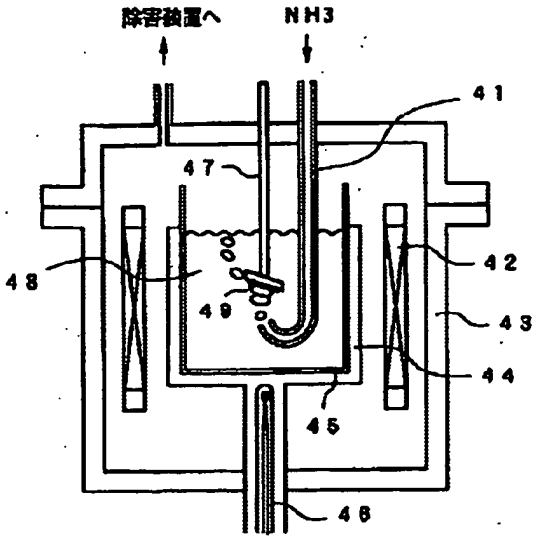
[Drawing 9]



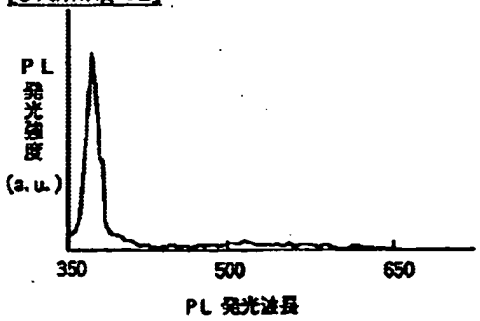
[Drawing 10]



[Drawing 11]



[Drawing 12]



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